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# Porcelains Within the Beryllia Field of the System Beryllia-Alumina-Zirconia

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The general physical properties of practically impervious porcelains within the beryllia (BeO) field of the system beryllia-alumina-zirconia ( $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$ ), whose base compositions approximate that of NBS Body No. 4811C, were found to be: maturing range, 1,500° to 1,600° C; apparent density, 2.9 to 3.4 g/cm<sup>3</sup>; shrinkage, 17.8 to 20.5 percent; room-temperature compressive strength, 238,000 to 305,000 lb/in.<sup>2</sup>; room-temperature transverse strength, 17,200 to 34,100 lb/in.<sup>2</sup>; room-temperature transverse strength after thermal shocking, 17,800 to 31,900 lb/in.<sup>2</sup>; transverse strength at 1,800° F (982° C), 15,100 to 25,100 lb/in.<sup>2</sup>; approximate Young's modulus at 1,800° F, 28,000,000 to 38,000,000 lb/in.<sup>2</sup>; relative thermal shock resistance, good; and Knoop hardness numbers (500-g load), 550 to 830. An admixture of 2 weight percent of calcia (CaO) to the base compositions of these porcelains (without which the specimens would not mature to an impervious structure) caused the appearance of unidentified isotropic phases.

## I. Introduction

Because of the advantageous high-temperature strength characteristics of "glass-free" bodies composed of the ceramic oxides, singly or in combination, as compared to similar strength properties of the metallic alloys, many refractory porcelains may be particularly well adapted for diversified uses in such power-plants as the gas-turbine and jet-propulsion engines.

Previous work at this Bureau [1, 2, 3],<sup>1</sup> at the Ohio State University Experiment Station [4], at the University of Illinois [5], and at the Lewis Flight Propulsion Laboratory of the National Advisory Committee for Aeronautics [6] has shown NBS Body No. 4811C [3], whose composition is within the system beryllia-alumina-zirconia ( $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$ ), to be outstanding in many high-temperature properties when compared with other refractory white-wares. Such comparisons made it seem advisable to investigate and report some of the physical properties of porcelains whose compositions approximate that of body 4811C.

A previous report [3] gives in some detail the phase relations of the system  $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$ . The failure of these oxide bodies to mature to nonporous structures was discussed in the Bureau report, but it was shown that the addition of small quantities of auxiliary fluxes to the base compositions did permit maturing of the bodies to a practically impervious condition. An addition of 4 percent of magnesia to body 4811, whose mole composition ratio is 48  $\text{BeO:1Al}_2\text{O}_3:1\text{ZrO}_2$ , caused the most pronounced

effect on the maturing range. Experience has shown that the use of magnesia tends to increase the particle sizes or distort the particle shapes and thereby to decrease the body strength. Considering all of the properties studied, an addition of 2 weight percent of calcia (CaO) produced the most satisfactory 4811 bodies, and this particular body composition is correctly designated as Body No. 4811C. All but one of the porcelain compositions given in this report contain a 2-percent addition of calcia to the base composition; the exception, for comparative purposes, is body 4811M, which contains an addition of 4 percent of magnesia.

## II. Materials and Equipment

The oxides used in the preparation of the test specimens were commercially available materials of high purity. The beryllia (BeO) was of nominal 99.7-percent purity, and spectrograms showed only traces of copper, iron, and magnesium, and very weak lines of silicon. Ground, washed, and sieved tabular alumina ( $\text{Al}_2\text{O}_3$ ) of 99.5-percent purity was supplied through the courtesy of the Champion Spark Plug Co. Commercial zirconia ( $\text{ZrO}_2$ ) of nominal 99-percent purity was recalcined at 1,440° C, after which spectrograms showed medium lines for niobium (columbium) and titanium, and only very weak lines or traces for calcium, copper, iron, magnesium, lead, and silicon. Calcia (CaO) was added as the pure chemically precipitated carbonate. As prepared for use, the materials were, in all instances, sufficiently finely divided to pass the No. 325 U. S. Standard Sieve. Comminution procedures have been given [7].

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

Firing of the test specimens for the determinations of maturing range and compressive strength was done in the NBS thoria-resistor furnace [8]. Figure 1 is a schematic cut-away drawing of the inner chamber of the furnace and shows three compression-test specimens, the supporting pedestals (thoria, zirconia, alumina, or beryllia), and one of eight heating elements. A Remmey high-temperature gas-fired kiln was used to mature the specimen bars for the thermal shock, transverse strength, and elasticity tests.

The apparatus used for the determination of the moduli of rupture and elasticity in flexure at elevated temperatures was designed by M. D. Burdick and has been described briefly [7]. The test furnace is constructed of lightweight insulating refractory brick, 2,600° F grade, within a shell of transite board. The chamber is 6 in. by 6 in. by 13 in. and is heated by means of six Globar elements. Power is supplied to the top, middle, and bottom pairs of Globars through three separate variable transformers. The specimen bar is supported on porcelain rockers (knife-edges) on dense firebrick of an appropriate thickness to locate the specimen at the center of the furnace chamber. Figure 2 shows the general construction features of the furnace (see also fig. 2 of [7]).

Load is applied to the top of the specimen at the quarter-points of the span through a loading bar and a ceramic yoke that extends through the furnace hearth to a third-order counterweighted lever. This lever was used to exert a downward pressure on the specimen. As it was desired to counterweight the lever to obtain a zero initial load, flexure plates rather

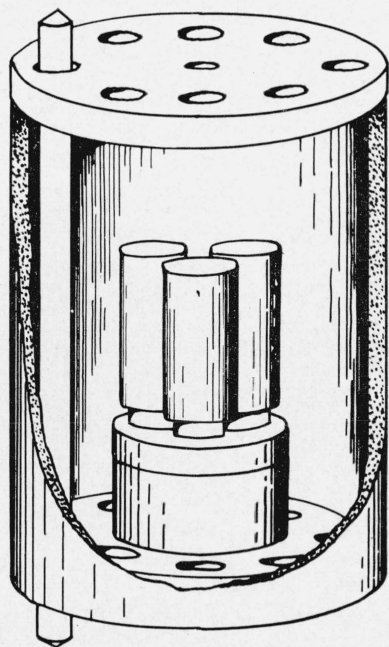


FIGURE 1. Resistor-furnace chamber.

This cut-away drawing of the inner chamber of the thoria-resistor furnace shows a typical arrangement for maturing three compression test specimens resting on platinum-rhodium disks. Also shown are the supporting pedestals of either beryllia, thoria, and alumina, and one of the eight thoria-resistor elements.

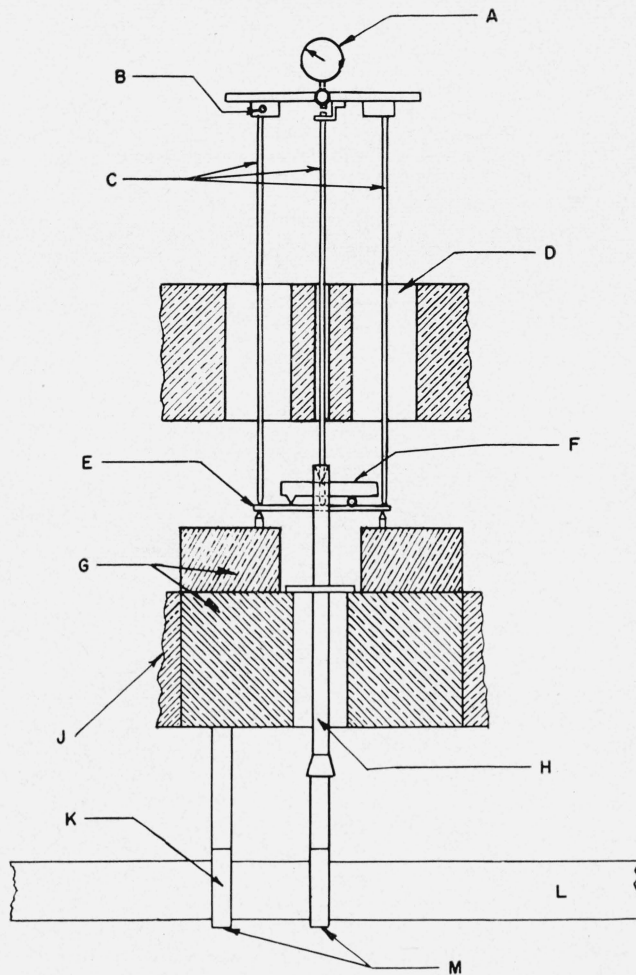


FIGURE 2. Transverse-strength test furnace.

This figure shows a section of the bending-strength test furnace indicating the specimen location, the loading arrangement, and the deflection measuring device. A, Dial gage; B, pivot; C,  $\frac{1}{8}$ -in. sapphire rods; D, narrow slot; E, specimen; F, loading bar (load applied at quarter points of span); G, dense fire brick; H, ceramic yoke; J, insulating brick; K, fulcrum; L, lever; M, flexure plates.

than a simple knife edge were used at the fulcrum of the lever system. Flexure plates were used also in attaching the yoke to the lever in order to maintain a constant lever ratio. The calibration of this lever was obtained by using the normal load-point,  $P$  (fig. 3, A) as the fulcrum, and determining the ratio of arms  $A$  and  $B$  by applying known weights at points  $F$  and  $L$ . If, for example, the ratio of  $B:A$  during calibration is found to be 14:1, the lever ratio during use as a third-class lever will be  $A+B:A=15:1$ . Quarter-point loading results in a bending-moment diagram, as shown by the solid line in figure 3, B. Applying the load at midspan would result in a bending-moment diagram, as shown by the broken line in the same figure. Quarter-point loading was used because, theoretically, the maximum stress is obtained for any fracture occurring between the two points of load application. The relative merits of the two types of loading have been discussed by Bobrowsky [9].

Load was transmitted to the specimen through a knife edge, which is an integral part of the loading

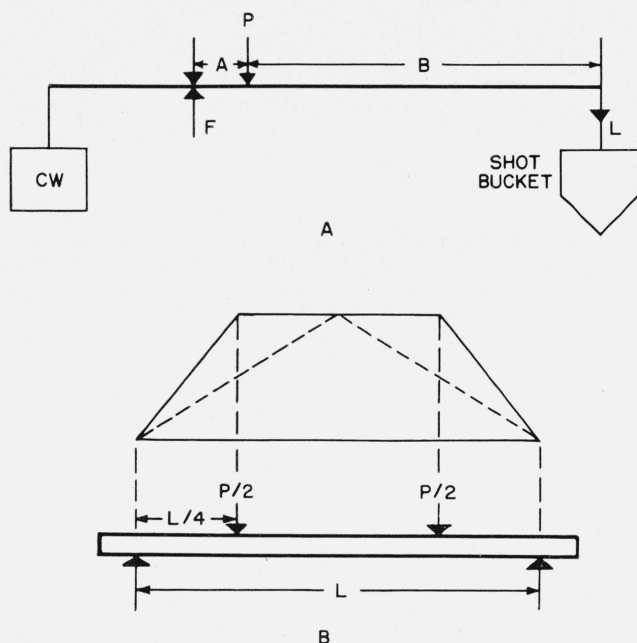


FIGURE 3. Mechanics of the lever-arm ratio and of quarter-point loading.

At A is shown the diagram for the calibration of the lever-arm ratio. If the ratio of B to A, during calibration as a first-class lever (fulcrum at P), is found to be 14:1, the lever-arm ratio during use as a third-class lever (fulcrum at F) will be  $(A+B):A = (1+14):1 = 15:1$ . At B is shown the bending-moment diagram resulting from quarter-point loading (solid line) and the bending-moment diagram resulting from single-point (midspan) loading (broken line).

bar, and through a sapphire rod. The rocker-type supports, and the rod and the loading knife edge, permit the use of a single loading bar for specimens of various spans and prevents torsional and axial forces. The deflection of the specimen at midspan is measured by means of a dial gage located directly over the specimen, but outside of the furnace. The gage, clamped to a rigid bar (fig. 2), is supported by two  $\frac{1}{8}$ -in. diameter artificial sapphire rods, the lower ends of which rest on the top of the specimen at the ends of the span. A third sapphire rod is used to actuate the stem of the dial gage. The rod rests on the specimen at midspan, passes through a slot in the loading bar, a hole in the yoke, and a hole in the furnace top. The hot junctions of the base-metal thermocouples are located so that one is above and the other is below the specimen, as near its center as possible.

The apparatus is designed to test specimens at spans of from 3 to 6 in. Slots are provided in the furnace top to permit various spacings between the outer sapphire rods, and one of these rods is attached to the gage-supporting bar through a pivot joint, which permits the bottom end of the rod to follow the shortening of the top of the specimen bar during deflection. A loading bucket is suspended from the end of the long arm of the lever, and lead shot is added to the bucket from a hopper equipped with a solenoid-operated sliding valve for manually starting or stopping the shot flow. In addition, a limit-switch is located under the lever to actuate the solenoid, stopping the flow when the specimen fails.

In order to permit deflection measurements at

known stresses, the shot is added by increments rather than continuously. Increments of weight, corresponding to a stress of about 1,500 lb/in.<sup>2</sup> on the specimen, are added to the lever at 2-min intervals, and the deflection is measured every minute. The values of the moduli of rupture and elasticity are computed from the equations

$$\text{Modulus of rupture} = \frac{3P_1L}{4bd^2}, \quad (1)$$

$$\text{Young's modulus of elasticity} = \frac{P_2a(3L^2 - 4a^2)}{4\Delta bd^3}, \quad (2)$$

where  $P_1$  is the total load on the specimen at failure;  $L$  is the span;  $b$  is the width of the specimen;  $d$  is the depth of the specimen;  $a$  is the point(s) of load application (a fraction of the span  $L$ ); and  $\Delta$  is the deflection at midspan corresponding to any load,  $P_2$ , below the elastic limit. When  $a$  is one-quarter of the span, the modulus of elasticity can be calculated from the equation

$$\text{Modulus of elasticity} = \frac{11P_2L^3}{64\Delta bd^3}. \quad (3)$$

In many instances, the accuracy of the values of Young's modulus reported for ceramic materials has been questioned when testing equipment similar to that described in this report was used. In order to determine whether this equipment would allow duplication of an accepted elasticity value, the Young's modulus of a bar of cold-rolled steel, whose size was almost identical to that of the ceramic specimens used, was determined (at various times) to be 29,400,000 lb/in.<sup>2</sup> This value is considered to be in good agreement with the accepted value of the modulus of elasticity of cold-rolled steel (30,000,000 lb/in.<sup>2</sup>  $\pm 5\%$ ).

### III. Methods

#### 1. Forming

In order to insure the desired reproducibility of results and to prevent segregation of the batch constituents during preparation of the specimens, the same compounding method was followed as has been described previously [7]. Briefly, the procedure entails weighing the constituent materials on a semi-analytical balance to  $\pm 0.005$  g, blunging with a laboratory-type variable-speed mixer with distilled water and a wetting agent, drying, sieving, and re-mixing with a starch binder.

Specimens for the investigation of the maturing range ( $\frac{5}{8}$  in. high by  $\frac{5}{8}$  in. in diam) and for the compression tests ( $1\frac{1}{4}$  in. high by  $\frac{5}{8}$  in. in diam) were pressed at 9,400 lb/in.<sup>2</sup> The thermal shock and transverse strength test bars ( $\frac{5}{16}$  in. thick by  $\frac{3}{4}$  in. wide by  $6\frac{1}{8}$  in. long) were pressed at 6,500 lb/in.<sup>2</sup> All of the specimens were formed in molds made of case-hardened steel and of oil-hardened nondeforming tool steel. The molds were lightly lubricated with a water-emulsifying oil before each specimen was made.



## 2. Testing

All of the test methods employed have been described previously [3 and 7] but, for the convenience of the reader, they are given briefly again. Carbon tetrachloride was used for the absorption determinations, and the results were converted to equivalent water absorption values. Matured bodies were considered to be those having less than 0.1 percent of equivalent water absorption. Shrinkage values were calculated from micrometer measurements both before and after heating. Apparent density values were obtained by calculations based on micrometer measurements and the weight of the dry specimens. The ends of the specimens for the compressive-strength tests were ground parallel, so that the length-to-diameter ratio of the test specimens was approximately 2. The test pieces were placed between cold-rolled steel blocks, and the compressive stress was applied at a loading rate of about 31,000 (lb/in.<sup>2</sup>)/min by a 75,000-lb hydraulic press. Ten cycles of quenching from 1,700° F (931° C) to room temperature by an air-blast (20° to 30° C) constituted the thermal shock test, and those bars surviving this quenching were tested for modulus of rupture in bending at room temperature. Comparable values for the modulus of rupture were determined also for specimens that had not been thermally shocked. The moduli of rupture and of elasticity at 1,800° F (982° C) were determined by using the furnace described. When it was noted that the deflection following loading continued after the first minute, it was assumed that permanent deformation, or "plastic flow", was occurring. This deformation could be verified when the test pieces were examined for permanent curvature following rupture. Plastic flow was not reported for body 4811C in a previous study [2] when an older testing furnace was used [10]. In order to investigate further the relative magnitude of the deformation, halves of bars broken in the hot bending tests were reground to about 1/8-in. thickness and the transverse strength test repeated by using a minimum span of 3 in. Loads of 12,000, 15,000, and 18,000 lb/in.<sup>2</sup> were maintained for 15 min, or until rupture occurred, during which times the deflection was measured at regular intervals.

## IV. Results

The base compositions of all of the porcelains studied in this investigation are contained within the beryllia field of the system beryllia-alumina-zirconia. The addition of 2 weight percent of calcia (CaO) to each of the base compositions, except body 4811M, which contains an admixture of 4 weight percent of magnesia (MgO), apparently does not affect primary crystallization to an extent distinguishable by petrographic examination. The base compositions of the bodies are given triaxially in figure 4 and numerically in tables 1 and 2.

It was found that all of the specimens could be matured (an absorption of less than 0.1 %) when heated for 1 hour at temperatures between 1,500°

and 1,600° C. Optimum maturity in the electric furnace was obtainable at either 1,500° or 1,550° C, and in the gas-fired furnace at 1,575° C. At optimum maturity the values for absorption were between 0.01 and 0.05 percent, the values for shrinkage were between 18.10 and 20.54 percent, and the apparent density ranged from 2.93 and 3.36 g/cm<sup>3</sup>.

It was suspected from the surface appearance of the matured specimens that certain of the porcelains would contain objectionably large grains. Petrographic examination, however, failed to reveal any excessive grain growth in any of the bodies, and the average grain sizes were found to be about 8 to 15  $\mu$  for the beryllia crystals, 8 to 15  $\mu$  for those of alumina, and from 2 to 8  $\mu$  for the zirconia. Occasional grains of beryllia, up to 80 to 100  $\mu$  in size, were noted in a few specimens. Although no changes were observed in the component crystal sizes of the 4811M body, a singular difference was noted in the shape of the beryllia crystals. In body 4811M, the BeO invariably occurred as rounded grains, whereas in all of the calcia-containing bodies the BeO was in the form of irregular, lath-shaped crystals.

High compressive strengths at room temperature were exhibited by all of the porcelains. The values ordinarily were about 275,000 lb/in.<sup>2</sup>, but two bodies, *I* and *J*, have strengths of 302,000 and 305,000 lb/in.<sup>2</sup>, respectively. Table 1 gives the data for maturing range, properties at maturity, and the compressive strength results determined for the porcelains investigated. Only the compressive strength values of the specimens that broke sharply into small fragments are included in this table. The values for those specimens that had splintered or cracked during the test were discarded. A method of specimen "seating", which practically eliminates splintering, is currently being employed,

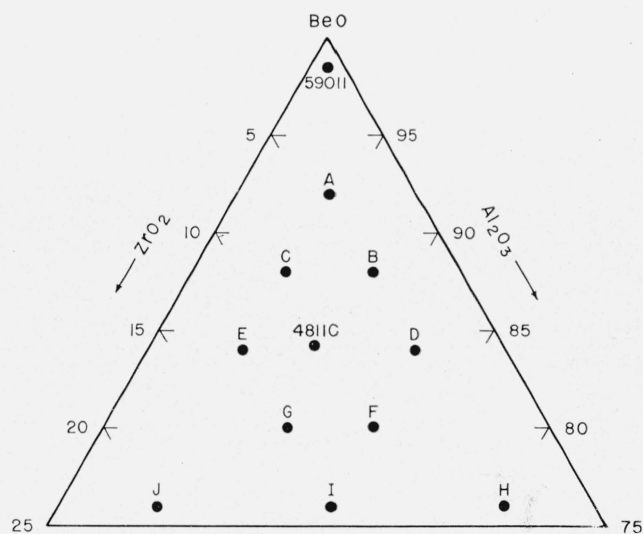


FIGURE 4. Base compositions of some porcelains within the system BeO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>.

Shown are the locations of the base composition (in weight percent) of the 13 beryllia porcelains discussed in this report. All but one of the body compositions contained an admixture of 2 weight percent of calcia (CaO); body 4811M contained 4 weight percent of magnesia.



TABLE 1. *Maturing range studies and compressive strength results*<sup>a</sup>

All bodies could be matured to practically imperviousness at temperatures between 1,500° and 1,600° C.

Body	Base composition <sup>b</sup>			Properties at maturity					Properties of compressive strength specimens <sup>c</sup>						
	BeO	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Test	Temperature	Shrinkage	Absorption	Apparent density (±0.01)	Test	Temperature	Shrinkage	Absorption	Apparent density (±0.01)	Height/diameter ratio <sup>d</sup>	Strength at room temperature <sup>e</sup> (±5,000 lb./in. <sup>2</sup> )
	%	%	%		° C	%	%	g/cm <sup>3</sup>		° C	%	%	g/cm <sup>3</sup>		lb/in. <sup>2</sup> 259×10 <sup>3</sup>
A-----	92.00	4.00	4.00	599-L	1,550	20.00	0.01	2.99	630-L	1,550	20.16	0.01	3.00	1.98	276
B-----	88.00	8.00	4.00	599-L	1,550	19.20	.02	3.04	627-L	1,550	19.74	.00	3.03	2.00	286
C-----	88.00	4.00	8.00	604-L	1,500	19.68	.01	3.07	629-L	1,500	19.58	.01	3.10	2.00	272
D-----	84.00	12.00	4.00	600-L	1,500	19.36	.02	3.08	625-L	1,500	19.58	.02	3.05	2.00	281
E-----	84.00	4.00	12.00	599-L	1,550	20.32	.02	3.18	621-L	1,550	19.58	.02	3.11	1.98	289
F-----	80.00	12.00	8.00	604-L	1,500	19.20	.01	3.10	631-L	1,500	20.54	.58	3.18	1.99	281
G-----	80.00	8.00	12.00	600-L	1,500	19.36	.02	3.21	634-L	1,500	20.22	.03	3.21	2.00	268
H-----	76.00	20.00	4.00	605-L	1,550	18.72	.01	3.10	629-L	1,550	19.10	.01	3.14	1.92	302
I-----	76.00	12.00	12.00	605-L	1,550	19.20	.01	3.21	628-L	1,550	19.58	.00	3.22	1.94	305
J-----	76.00	4.00	20.00	605-L	1,550	20.00	.01	3.30	632-L	1,550	20.54	.00	3.36	2.00	240
59011 <sup>g</sup> -----	98.50	0.68	0.82	-----	-----	-----	-----	-----	635-L	1,600	19.90	.03	2.91	2.00	251
4811C-----	84.21	7.15	8.64	599-L	1,550	19.36	.01	3.08	-----	1,550	-----	-----	-----	-----	238
4811M-----	84.21	7.15	8.64	536-L	1,600	18.10	.01	3.09	543-L	1,600	17.79	.00	3.16	1.93	-----

<sup>a</sup> Values obtained for specimens matured in an electric furnace for 1 hr at the temperatures specified.<sup>b</sup> All but one of the bodies contain an admixture of 2% of calcia to the base composition; body 4811M contains an admixture of 4% of magnesia.<sup>c</sup> Unless otherwise indicated, the values given are the averages for three test specimens.<sup>d</sup> Specimens were about 1 in. high by ½ in. in diameter.<sup>e</sup> Compression testing was done at a constant loading rate of about 31,250 lb/in.<sup>2</sup> by using cold-rolled steel blocks for platen protection. The value given is the average of two specimens (three were broken, but one had splintered and the value was discarded).<sup>f</sup> See footnote e. Value given is for one specimen (three were broken, but two had splintered and the values were discarded).<sup>g</sup> This body (no admixture to the composition given) reported on by the Battelle Memorial Institute (private communication). See also table 2, footnote f.<sup>h</sup> R. F. Geller, et al., J. Research NBS **36**, 277, (1946) RP1703.TABLE 2. *Strength in bending and elasticity values*<sup>a</sup>

All bars survived ten cycles of test for thermal shock resistance (from 1,700° F (931° C) to room temperature by an air blast)

Body	Base composition <sup>b</sup>			Maturing data			Strength in bending (flexure) at— <sup>c</sup>			
	BeO	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Test	Temperature	Absorption	Room temperature		1,800° F (982° C)	
							Not thermally shocked	After thermal shocking	(±2,000 lb/in. <sup>2</sup> )	Young's modulus <sup>d</sup> (±3,000,000 lb/in. <sup>2</sup> )
	%	%	%		° C	%	lb/in. <sup>2</sup>	lb/in. <sup>2</sup>	lb/in. <sup>2</sup>	lb/in. <sup>2</sup>
A-----	92.00	4.00	4.00	33-R	1,575	0.01	31.2×10 <sup>3</sup>	25.8×10 <sup>3</sup>	20.5×10 <sup>3</sup>	30×10 <sup>6</sup>
B-----	88.00	8.00	4.00	33-R	1,575	.01	31.0	25.5	19.0	36
C-----	88.00	4.00	8.00	33-R	1,575	.01	26.7	23.4	19.6	33
D-----	84.00	12.00	4.00	33-R	1,575	.02	27.6	26.9	16.8	28
E-----	84.00	4.00	12.00	31-R	1,575	.01	26.7	25.5	20.7	32
F-----	80.00	12.00	8.00	35-R	1,575	.02	25.8	25.2	18.2	31
G-----	80.00	8.00	12.00	35-R	1,575	.02	25.7	23.5	17.3	36
H-----	76.00	20.00	4.00	31-R	1,575	.03	30.2	25.0	18.9	32
I-----	76.00	12.00	12.00	32-R	1,575	.25	27.2	26.8	19.9	37
J-----	76.00	4.00	20.00	32-R	1,575	.04	30.4	29.5	25.1	36
59011 <sup>g</sup> -----	98.50	0.68	0.82	32-R	1,575	3.5	18.7	19.9?	16.4	31
4811C-----	84.21	7.15	8.64	35-R	1,575	0.01	34.1	31.9	21.4	36
4811C <sup>f</sup> -----	84.21	7.15	8.64	-----	-----	about 0.2	-----	-----	18.4	42
4811C <sup>g</sup> -----	84.21	7.15	8.64	-----	-----	about 0.2	25.2	24.1	13.8	21
4811M-----	84.21	7.15	8.64	34-R	1,600	1.7	17.2	17.8	15.1	38

<sup>a</sup> Values obtained for specimens matured in a gas-fired furnace for 1 hour at the temperatures specified.<sup>b</sup> All but one of the bodies contain an admixture of 2% of calcia to the base composition; body 4811M contains an admixture of 4% of magnesia.<sup>c</sup> Two test bars, about 5½ in. by ½ in. by ¼ in., of each composition were broken at room temperature, two were thermally shocked and then broken at room temperature, and three were broken for the transverse strength and elasticity tests at 1,800° F (982° C).<sup>d</sup> The modulus of elasticity values (Young's modulus) are considered as only relative because they were calculated from the curve of the deformation versus load at the lowest part of the curve where the plastic flow was small.<sup>e</sup> This composition (containing no admixtures) reported on by the Battelle Memorial Institute (private communication) as follows: After heating for 3 hours at 3,100° F (1,740° C), the body showed an apparent porosity of 14%, had a bulk density of 2.56 g/cm<sup>3</sup>, and showed a room temperature transverse strength of 18,600 lb/in.<sup>2</sup><sup>f</sup> Specimens of body 4811C prepared for another investigation (footnote g), but tested for moduli of rupture and elasticity at 1,800° F in the new transverse strength test furnace.<sup>g</sup> Values given in NACA report W-48 (June 1946), R. F. Geller and M. D. Burdick.

although it was not used for the test specimens of this investigation.

These porcelains are fairly resistant to thermal stresses as evidenced by their ability to withstand 10 cycles of shocking from 1,700° F (931° C) to room temperature by an air blast (20° to 30° C).

Their transverse strengths after shocking were usually slightly lower (18,000 to 32,000 lb/in.<sup>2</sup>) than the values obtained for comparable specimens that had not been shocked (17,000 to 34,000 lb/in.<sup>2</sup>). Considerably lower strengths in bending (15,000 to 25,000 lb/in.<sup>2</sup>) were noted for all of the matured

porcelains at 1,800° F (982° C), compared to their strengths at room temperature.

From the viewpoint of transverse strength at room temperature the outstanding body was 4811C, although a loss in strength of 2,000 lb/in.<sup>2</sup> was noted as the result of thermal shocking. If the effect of heat shock on the transverse strength is chosen as the basis of comparison, the outstanding bodies were 4811M, I, F, D, and J. Only bodies 4811C and J, however, had transverse strengths after heat-shocking of about 30,000 lb/in.<sup>2</sup>; the other bodies ranged as low as 17,800 lb/in.<sup>2</sup> The strongest body in the bending tests at 1,800° F (982° C) was J. Its value of 25,000 lb/in.<sup>2</sup> was about 20 to 25 percent higher than those of the next strongest bodies, 4811C, E, and A.

During the determinations of the moduli of rupture and elasticity at 1,800° F, it was noted that body 4811C and others exhibited plastic deformation. Although the modulus of elasticity values at 1,800° F are reported, they must be considered as only relative, because they were calculated from the curve of the deformation versus load at the lowest part of the curve where plastic flow was relatively small. Table 2 gives the results of the tests of thermal shock, transverse strength at room temperature both before and after heat-shocking, and the moduli of rupture and elasticity at 1,800° F (982° C).

In order to obtain some indirect measure of the deformation-under-load (plastic flow) that occurred during the original tests of rupture and elastic strengths, half-bars of some of the body compositions used for hot transverse strength test (which allowed a minimum 3-in. span) were reground to a thickness of  $0.1250 \pm 0.0007$  in. The deflection was measured at 1,800° F (982° C) at 1-min intervals for 15 min under loads of approximately 12,000, 15,000, and

18,000 lb/in.<sup>2</sup>, or until rupture had occurred. Figure 5 shows the results of these tests. Table 3 gives the strain-rate data determined from the stress-strain tests and, for correlation purposes, a listing of the hardness, strength, and elastic properties of all of the porcelains of this study is also given.

Examination of table 3 reveals that there is no correlation between the strain rate at 1,800° F and the strength properties of the various porcelains. The very low hardness of body 59011 (whose hardness would be expected to approximate that of BeO) is probably due largely to the porous condition of the test specimen. In addition, considerable difficulty was encountered in obtaining suitably polished surfaces for all of the specimens, and it is con-

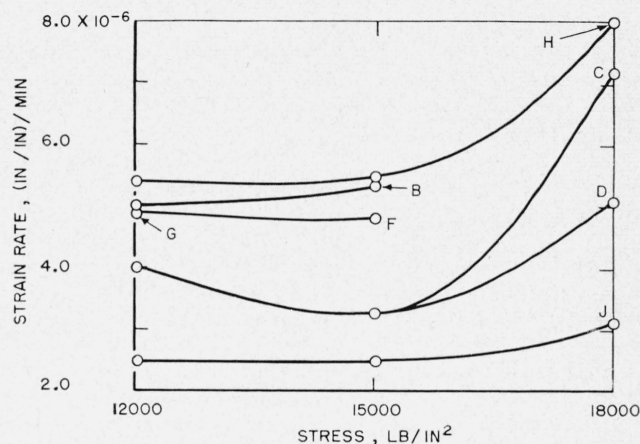


FIGURE 5. Short-time stress-strain relations of some beryllia porcelains.

Shown are the strain rates at 1,800° F (982° C) of seven beryllia porcelains when maintained for 15 min at each of three stresses, or until rupture occurred.

TABLE 3. Strength, stress-strain, and Knoop hardness values

Strength at room temperature					Strength at 1800° F (982° C) <sup>a</sup>					Strain rates <sup>b</sup>				Knoop hardness <sup>c</sup>		
Compressive strength <sup>d</sup>		Transverse strength <sup>a</sup>			Transverse strength		Young's modulus <sup>e</sup>	Maximum strain at fracture		Body	12,000-lb/in. <sup>2</sup> stress	15,000-lb/in. <sup>2</sup> stress	18,000-lb/in. <sup>2</sup> stress	Body	10 indentations at 500-g load	
Body		Body	Not thermally shocked	After thermal shocking	Body			Calculated <sup>f</sup>	Observed <sup>f</sup>						Average	Range, low to high
	lb/in. <sup>2</sup>		lb/in. <sup>2</sup>	lb/in. <sup>2</sup>		lb/in. <sup>2</sup>	lb/in. <sup>2</sup>				(in./in.)/min	(in./in.)/min	(in./in.)/min		K <sub>500</sub>	K <sub>500</sub>
J.....	305×10 <sup>3</sup>	4811C	34.1×10 <sup>3</sup>	31.9×10 <sup>3</sup>	J	25.1×10 <sup>3</sup>	36×10 <sup>6</sup>	0.70×10 <sup>-3</sup>	21×10 <sup>-3</sup>	H	5.4×10 <sup>-6</sup>	5.5×10 <sup>-6</sup>	8.0×10 <sup>-6</sup>	J	830	700 to 900
I.....	302	A	31.2	25.8	4811C	21.4	36	.59	18	B	5.0	5.4	-----	F	810	740 to 880
F.....	289	B	31.0	25.5	E	20.7	32	.65	21	F	4.9	4.8	-----	E	810	760 to 920
G.....	286	J	30.5	29.5	A	20.5	30	.68	28	G	4.9	-----	-----	H	810	700 to 900
C.....	281	H	30.2	25.0	I	19.9	37	.54	13	C	4.0	3.3	7.2	4811M	810	710 to 960
E.....	281	D	27.6	26.9	C	19.6	33	.60	18	D	4.0	3.3	5.1	A	800	760 to 900
B.....	276	I	27.2	26.8	B	19.0	36	.53	16	J	2.5	2.5	3.1	C	800	700 to 900
D.....	272	E	26.7	25.5	H	18.9	33	.58	13	-----	-----	-----	-----	B	800	600 to 900
H.....	268	C	26.7	23.4	F	18.2	31	.58	16	-----	-----	-----	-----	G	790	720 to 880
A.....	259	F	25.8	25.2	G	17.3	36	.48	15	-----	-----	-----	-----	D	780	710 to 840
4811C.....	251	G	25.7	23.5	D	16.8	28	.60	20	-----	-----	-----	-----	I	780	670 to 900
59011.....	240	59011	18.7	19.9?	59011	16.4	31	.53	15	-----	-----	-----	-----	4811C	760	670 to 840
4811M.....	238	4811M	17.2	17.8	4811M	15.1	38	.40	12	-----	-----	-----	-----	59011	550	420 to 770

<sup>a</sup> The maturing data for the specimens used in these tests are given in columns 5 to 7 of table 2.

<sup>b</sup> One half-bar of each composition from the transverse strength tests at 1,800° F, which allowed a minimum span of 3 in., was reground for this test.

<sup>c</sup> Knoop numbers determined by using a solenoid-operated Tukon tester and a 500-g load. For comparison, a specimen of beryllia (BeO) that had been used as a pedestal in the thoria-resistor furnace had an average Knoop hardness of  $K_{500}=1,030$  (980 to 1,110).

<sup>d</sup> The maturing data and other physical properties of these test specimens are given in columns 11 to 17 of table 1.

<sup>e</sup> Young's modulus values are considered as being only relative because they were calculated from the deformation-load curve at the lowest part where the "plastic flow" was relatively small.

<sup>f</sup> The maximum strain (deformation) at fracture was calculated by dividing the value of the modulus of rupture by that of the modulus of elasticity.

sidered, therefore, that the Knoop hardness values obtained are lower than they should be.

Petrographic examination of the specimens after the bending tests revealed either one or two isotropic phases in all of the test bars, except those of body 4811M. These phases were present also in the test bars made for use in the preliminary study of the tensile and creep properties of porcelains [1]. Unfortunately for identification purposes, these phases appeared as very thin films, usually less than  $\frac{1}{2}\mu$  in thickness, interstitial to and surrounding the beryllia grains. It was possible to identify only their refractive indices, which, in some cases, were considerably above 1.73 and, in others, below 1.71. Reexamination of some of the older specimens and test pieces from the studies of maturing range and compression strength revealed that the isotropic phases were present in the same relative proportions as were noted for the transverse strength specimens. There seemed to be somewhat more of these phases in the bodies matured in the gas-fired furnace than in the bodies matured in the thoria-resistor furnace. Although it was possible to establish the presence of the isotropic phases in the various test specimens, no quantitative correlation between the amounts of the isotropic phases present and the relative order of the strengths of these porcelains (table 3) could be determined. Generally, however, it was found that the order of the bodies according to their estimated content of these phases was H, B, F, G, C, D, E, 4811C, and J. Body H usually contained the most of these phases and, in all instances, none were found in body 4811M.

A number of unsuccessful attempts were made to determine the nature of the isotropic phases. In order to examine the porcelains by reflected light with the metallographic microscope, satisfactorily polished and etched specimen surfaces are required. These surfaces were not obtained by the use of any of the common abrasives, including diamond powders, nor by the use of any of the ordinary etching solutions, including a previously successful electrolytic etching method. The inability to obtain suitably finished surfaces also made it impossible to obtain satisfactory shadowed surface replicas for study with the electromicroscope.

## V. Discussion

One of the results of this investigation was the finding that the addition of 2 weight percent of calcia (CaO) to the  $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$  porcelains caused one or more isotropic phases to appear in the matured specimens. Whether these phases are crystalline or glassy has not been determined. An admixture of 4 weight percent of magnesia (MgO) to one of the base compositions caused no observable additional phase.

Although no identification of the isotropic phases could be made, there is some basis for speculation as to their probable compositions. Two binary systems,  $\text{CaO-Al}_2\text{O}_3$  [11] and  $\text{CaO-BeO}$  [12], contain appreciable areas of complete melting at temperatures below those at which the porcelains of this study

were matured. In the first system,  $\text{CaO-Al}_2\text{O}_3$ , isotropic crystalline phases are known to exist [13]. They are the compound  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  with a refractive index of 1.710, the compound  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  with indices of 1.608 and 1.662 depending upon the crystallization behavior, and an unstable prismatic phase, whose indices are 1.687 and 1.692 (very weak birefringence). A glass of refractive index 1.68, a crystalline phase with an index of 1.684, and an unidentified isotropic phase of index of 1.668 are known for one mixture in the system  $\text{CaO-Al}_2\text{O}_3\text{-BeO}$  (42% of CaO, 41% of  $\text{Al}_2\text{O}_3$ , and 17% of BeO). At a temperature of  $1,450^\circ\text{C}$  this mixture was completely liquid.

Two isotropic phases were identified in the porcelains investigated in this study. One of these had an index considerably above 1.73 and the other somewhat below 1.71. For the first of these two phases, it is conceivable that either a beryllium calcium zirconate or an aluminum calcium zirconate had been formed, the calcia and zirconia combining first to form a high index cubic zirconia solid solution ( $n=2.08$ ), and then reacting in the presence of either or both of the other oxides to form an isotropic crystalline phase, an isotropic mixed crystal series, or a glass. The second of the unidentified phases is likely to be one of the isotropic crystalline phases contained within the system  $\text{CaO-Al}_2\text{O}_3$ .

As previously stated, there were not sufficient data available for a study of the correlations that might exist between the amounts of the isotropic phases present and the test values of the various strength properties of these porcelains. Even though an additional boundary phase is present, the strengths of these calcia-containing bodies compare favorably with those of other oxide porcelains, such as the bodies of the systems  $\text{MgO-BeO-ZrO}_2$ ,  $\text{MgO-BeO-ThO}_2$ ,  $\text{MgO-BeO-Al}_2\text{O}_3$ , and  $\text{BeO-Al}_2\text{O}_3\text{-ThO}_2$  (tables 1 and 9 of [7]).

## VI. Conclusions

The general physical properties of practically impervious porcelains within the beryllia field of the system  $\text{BeO-Al}_2\text{O}_3\text{-ZrO}_2$ , whose base compositions approximate that of NBS Body No. 4811C, were found to be: maturing range,  $1,500^\circ$  to  $1,600^\circ\text{C}$ ; apparent density, 2.9 to  $3.4\text{ g/cm}^3$ ; shrinkage, 17.8 to 20.5 percent; room temperature compressive strength, 238,000 to 305,000  $\text{lb/in.}^2$ ; room temperature transverse strength, 17,200 to 34,100  $\text{lb/in.}^2$ ; room temperature transverse strength after thermal shocking, 17,800 to 31,900  $\text{lb/in.}^2$ ; transverse strength at  $1,800^\circ\text{F}$  ( $982^\circ\text{C}$ ), 15,100 to 25,100  $\text{lb/in.}^2$ ; approximate Young's modulus at  $1,800^\circ\text{F}$  (see discussion), 28,000,000 to 38,000,000  $\text{lb/in.}^2$ ; relative thermal-shock resistance, good; and Knoop hardness numbers (500-g load), 550 to 830.

For an all-ceramic body exhibiting high strengths both at room temperature and at  $1,800^\circ\text{F}$  ( $982^\circ\text{C}$ ) and good thermal shock resistance, it is suggested that the possibilities apparent in body J be further investigated. The base composition of this body is



76 percent of beryllia ( $\text{BeO}$ ), 4 percent of alumina ( $\text{Al}_2\text{O}_3$ ), and 20 percent of zirconia ( $\text{ZrO}_2$ ), with an admixture of 2 weight percent of calcia ( $\text{CaO}$ ). This body becomes practically impervious at temperatures between  $1,500^\circ$  and  $1,600^\circ \text{C}$  in both electric and gas-fired furnaces, with a resultant shrinkage of about 20 percent and an apparent density of about  $3.3 \text{ g/cm}^3$ .

The results of this study indicate that some of the porcelains within the beryllia field of the system beryllia-alumina-zirconia may be of use as components for various heat engines where high strength and some degree of elasticity, rather than the ultimate in refractoriness, are desired.

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# Some Electrical Relations in Galvanic Couples<sup>1</sup>

By H. D. Holler

The electrical relations are developed for a galvanic couple (short-circuited cell) with and without polarization by externally applied current. Their significance in the derivation of criteria for cathodic protection is demonstrated. The mechanism of current flow between couples at different potentials is explained. The importance of galvanic-couple theory in governing current distribution over an electrode surface is indicated.

## I. Introduction

In the study of electrode processes, an understanding of the electrical relations in galvanic couples and of their behavior toward externally applied current is essential. It has, of course, been known since the time of Galvani and Volta, that a bimetallic junction in contact with an electrolyte is a source of electromotive force and current. While there is some question regarding the exact source of the emf, it can be shown by thermodynamics that the chemical potential of such a system manifests itself as an emf, theoretically capable of delivering current.

In accordance with Nernst's law, it is also well known that an emf may exist between two areas of the same metal, each in different environments, and a galvanic current will flow when they are metallicly connected. Even in the case of a pure metal, in an electrolyte, galvanic currents may flow between its different crystal faces, from cracks in its surface to surrounding areas, or between areas in different

states of oxidation. As a result, the conditions favoring the existence of galvanic couples in the phase boundary are nearly always fulfilled whenever a metal comes into contact with an electrolyte. In connection with the "local-cell" theory of corrosion, some of the electrical relations governing these currents have been derived by Müller, Akimow, and Thomasow, and others [1].<sup>2</sup> There are galvanic circuits of all magnitudes ranging from those of molecular dimensions to those of great size existing underground. They are present, to some extent, on the electrodes in practically all electrochemical processes. Systems of several electrodes have been studied by many workers including Brown and Mears, Landau and Petrocelli [2].

While thermodynamics defines the driving force of an electrochemical reaction, the rate of the latter is controlled by irreversible factors, represented by polarization, as defined in its broadest sense; that is, including resistive potential differences also. Sometimes, as in electric batteries, it is desirable that the polarization resulting from delivery of current to an

<sup>1</sup> The term "galvanic couple" or "couple" is used in this paper for the sake of brevity and means a galvanic cell having its electrodes metallicly connected through an external resistance that may be negligibly small.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.